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(54) Title: BENZOIC ACID ESTERS AS COALESCING AGENTS FOR PAINT COMPOSITION

(57) Abstract

This application discloses the use of esters of benzoic acid having from about 10 to about 12 carbon atoms in the ester moiety as coalescent agents for paint compositions and for use in the preparation of plastisols and caulks.

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BENZOIC ACID ESTERS AS COALESCING AGENTS FOR PAINT COMPOSITION

Background of the Invention

This invention relates to new monobenzoate esters. In particular, it relates to new esters useful as coalescing agents in paint formulations and also as plasticizers.

One of the desired qualities of paint is that they produce a uniform coating. In order to have the proper film formation, coalescent agents are incorporated into paint formulations. One of the commercial coalescing agents used in paint formulations is texanol. There is a need for additional coalescing agents since texanol does not impart the required characteristics to all paint formulations.

It is therefore an object of the present invention to devise new coalescing agents for paint formulations.

Other coalescing agents are taught in European Patent Application No. 80303088.1 by Friel ("Friel"). Friel discloses a coating composition comprising a water-insoluble addition polymer and an effective amount of a coalescing agent comprising an ester; the ester having a normal boiling point of from 160° to 290°C. Friel further teaches an ester where R^1 can be aryl and R^2 is preferably a 3 to 5 carbon atom group and specifically lists butyl benzoate as a preferred ester.

Another object of the present invention is to provide new coalescing agents which surpass the esters taught in Friel in significant properties.

Another object of the present invention is the preparation of latex formulations that are stable at a wide range of temperatures.

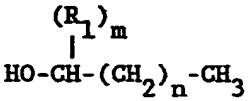
Still another object of the present invention is the creation of plasticizers having good compatibility with various resinous materials.

Other objects of the present invention will become apparent from the ensuing description.

Summary of the Invention

This invention is directed to the use of esters of benzoic acid having about 10 to about 12 carbon atoms in its ester moiety as a coalescing agent for paint compositions and in the manufacture of plastisols. In particular, it is preferred to use hydrocarbon esters of benzoic acids for these purposes.

The compounds of the present invention can be prepared by the reaction of benzoic acid and an aliphatic alcohol of the following structural formula:



(I)

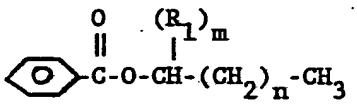
wherein R_1 is hydrogen or methyl;

when R_1 is hydrogen, then n is an integer from about 8 to about 10, when R_1 is methyl, then n is an integer from about 7 to about 9;

m is 1; and

when R_1 is hydrogen, then m+n is from about 9 to about 11, when R_1 is methyl, then m+n is from about 8 to about 10.

The preferred ester that is formed by this reaction has the following structral formula:



(II)

This reaction can be performed using standard esterification conditions, removing the water of reaction continuously as formed. An esterification catalyst is used to maximize yields. Examples of esterification catalysts which can be used include stanneous oxide, stanneous diacetate, monobutyl tin oxide, butyl tin tris 2-ethyl hexanoate, dibutyl tin diacetate, dibutyl tin oxide,

stannous benzoate, p-toluene sulfonic acid, sulfonic acid, phosphoric acid, hydrochloric acid, aluminum trichloride, methane sulfonic acid, tetraisopropyl titanate, zirconium carbonate and ion-exchange resins. Temperatures of up to about 250°C are sufficient. While the reaction is equimolar, it is preferred to use a slight molar excess of benzoic acid. Other reaction variables that can be used include the presence of an azeotrope such as cychlohexane, but are not necessary for the formation of the compounds of the present invention.

The following Examples 1-2 illustrate the preparation of the present compounds, but it is to be understood that the present compounds can be made by other procedures.

While Examples 1-2 only show the preparation of isodecyl benzoate, the same procedures can be used for the preparation of the other compounds of the present invention.

Examples 3-5 compare texanol with isodecyl benzoate, the preferred embodiment of the present invention.

Example 6 compares n-butyl benzoate as taught in Friel with isodecyl benzoate, the preferred embodiment of the present invention.

EXAMPLE 1

Preparation of Isodecyl Benzoate

Isodecyl alcohol (316 grams; 2 moles); benzoic acid (250 grams; 2.05 moles), toluene (100 ml) and para toluene sulfonic acid (2 grams) were placed into a glass reaction flask equipped with stirrer, thermometer, heating mantle, 12" column packed with 1/4" glass rings, Dean-Stark water trap, and condenser. The temperature increased from 26°C to 187°C as the reaction proceeded with stirring. Then the reaction mixture was cooled to 100°C. Soda ash (100 ml; 20% solution) was added to the mixture and was followed by the addition of a mixture of soda ash (50 ml; 20% solution) and chlorox (100 ml) at 81-100°C. The alkaline bottom layer was separated from the mixture. After the mixture was dried, the toluene was removed by heating the mixture to 178°C at

45 mmHg. The desired product (515 grams) was obtained after filtration, representing a yield of 98.3%.

EXAMPLE 2

Preparation of Isodecyl Benzoate

Isodecyl alcohol (791.4 grams; 5.-0 mol), benzoic acid (622.8 grams; 5.1 mol), zirconium carbonate (3.3 grams) and toluene (75 ml) were placed into a three-necked, round bottom flask equipped with stirrer, thermometer, 10" Vigeraux column, water trap and condenser. The reaction temperature was 184°C, washed first with water (25 mls) at 90-95°C for 30 minutes, then with sodium carbonate (15%) at 90-95°C for 30 minutes and twice with water (300 ml) at 90°C for five minutes. After being washed, the product was dried at 125°C and filtered to yield the desired product (1254.6 grams; 95.6% yield). It assayed 99.5% with the following properties:

Hydroxyl No.	7.8 mg KOH/gm
Color	30 APHA
Acidity	< 0.01%
Moisture	0.02%

Other compounds within the present invention include, but are not limited to, decyl benzoate, isoundecyl benzoate, undecyl benzoate, dodecyl benzoate and isododecyl benzoate. It has now been found that compounds of the structural formula (II) have excellent properties as coalescent agents in latex based paints. Coalescent agents perform an important function in paints in the formation of a continuous film at all temperatures of application of the paint. The amount of the coalescent agent in the paint will vary with the other components of the paint. Most latex paints are either acrylic or vinyl acrylic based products. In addition, the paints contain a variety of other components including pigments, binders, fillers, dispersants, thickeners and anti-freeze agents. The identity of these components is well known to paint formulators.

Generally the paint formula will contain from about 4 to about 12% by weight of the coalescent agent, although other

amounts can often be used. Normally, the coalescent agent can be added to the binder, filler, dispersant, thickeners and other additives by first making a slurry of such materials on a high speed mill and grinding the pigment on a high speed mill into the slurry. Then the coalescent agent can be added into the slurry on the high speed mill. Finally, the slurry can be let down into the latex on a low speed mixer.

In order to determine the effectiveness of the compounds of Formula (II) as coalescent agents, in Examples 3-5 the following tests of typical paint formulations containing isodecyl benzoate as the coalescent agent were performed comparing the benzoate esters of the present invention with a paint formulation containing texanol, a commercial coalescent agent.

EXAMPLE 3

The following tests were performed:

1. Viscosity: Determined by use of a Stormer Viscometer immediately after the paint formulation has been adjusted to room temperature.

2. Weight: Determined after the paint formulation has been adjusted to room temperature and stirred for 30 minutes.

3. Color: Panels were made with a 0.003 Bird Blade on Lenata White chart. Reflectance was read on Applied Color Spectra's Sensor at 540 mm.

4. Color Acceptance: Mixes were made using Nirodox yellow oxide and phthalo blue 888 colorants at a level of two ounces per gallon of paint and were shaken on a Red Devil Paint shaker for three minutes. Test panels were made by making a 0.003 Bird Blade drawdown and a brushout on a Lenata chart. Color differences of drawdown versus brushout were determined using Applied Color Systems' computer system.

5. Hiding Power: Contrast ratio was determined by first measuring reflectance on white and black are as taken from 0.003 Hard Blade drawdown on a Lenata opacity chart. The contrast ratio was calculated by dividing the reflectance on the black area by

the reflectance on the white area.

6. Sheen: Read hiding power panels on 60° and 85° Gardner Gloss Meter after 48 hours dry.

7. Porosity: Paints were checked according to ASTM D-3258-80 and the loss in reflectance determined and reported as the percent retained.

8. Freeze-Thaw: 1/4 pint samples of each paint were cycled for eight hours at -15°F and 16 hours at room temperature. The paints were checked after each cycle for five cycles.

9. Oven Stability: Determined change in viscosity of the paints after six days at 120°F.

10. Low Temperature Filming: 0.003 Bird Blade drawdowns were made on the backside of Lenata panels and dried 48 hours at 40°F. Panels were examined for cracks with 60x magnification.

The formulation was prepared by mixing the following ingredients for four minutes on a Cowles mill:

Component	Pounds	Gallons
Water	250.0	30.0
Ethylene Glycol	20.0	2.15
Colloid 643	2.0	0.27
Bioban CS-1135	2.0	0.24
Cellosize FR-1500	4.5	0.39
AMP-95	1.0	0.10
Colloid 224	5.0	0.50
Triton N-101	2.0	0.23
Tronox CR-800	220.0	6.77
Sanitone #1	110.0	5.02
Snowflake	120.00	5.33

Texanol and isodecyl benzoate were added to aliquots of the formulation to prepare a paint having the indicated percentage of coalescent agent by weight based on resin solids.

FORMULATION	TEXANOL			WATER		ISODECYL BENZOATE		
	Pounds	Gallons	%	Pounds	Gallons	Pounds	Gallons	%
1	9.9	1.25	6	5.1	0.61	0	0	0
2	0	0	0	8.6	1.03	6.6	0.83	4.0
3	0	0	0	5.1	0.61	9.9	1.25	6.0
4	0	0	0	0	0	14.9	1.87	9.0

FORMULATION	INITIAL VISCOSITY (K.U.)	WEIGHT (Lbs/Gal)	COLOR ACCEPTANCE	HIDING POWER	SHEEN 60°F	SHEEN 85°F	COLOR
1	83	11.68	0.37	0.9706	2	3	91.19
2	78	11.68	0.27	0.9730	2.5	3	91.32
3	77	11.68	0.33	0.9763	2	3	91.37
4	81	11.68	0.31	0.9804	2.5	3	91.19

	POROSITY % Retained	FREEZE THAW	OVEN STABILITY (% Decrease) In Viscosity
1	95.91	Passed	3.61
2	95.76	Passed	7.69
3	95.71	Passed	8.97
4	97.27	Passed	7.50

EXAMPLE 4

Additional tests were performed on a second set of paint formulations containing texanol and isodecyl benzoate, as follows:

1. Viscosity: Determined using ASTM procedure D-562.
2. Package Stability: Determined using ASTM procedure D-1849.
3. Washability: Determined using ASTM procedure D-3450.
4. Scrub Resistance: Determined using ASTM procedure D-2486.

The following formulation was prepared:

	Pounds
Water	250.0
Ethylene Glycol	20.0
Colloid	2.0
Bioban CS-1135	2.0
Cellosize ER-1500	4.5
AMP-95	1.0
Colloid-224	5.0
Triton N-101	2.0
Tronox CR-800	220.0
Sanitone #1	110.0
Snowflake	120.0

Texanol and isodecyl benzoate were mixed into aliquots of this formulation. 9.9 pounds of texanol and 9.9 pounds of isodecyl benzoate were mixed into aliquots of this formulation to

prepare formulations 5 and 6 each containing six percent by weight of the respective coalescent. Then the following ingredients were mixed into each formulation to prepare the test paint formulations:

Component	Pounds
UCAR 367	301.0
Colloid 643	2.0
Water	113.4

The two paint formulations were tested with the following results:

FORMULATION	VISCOSITY (KU)		WASHABILITY	SCRUB RESISTANCE
	Initial	2 Weeks @ 125°F	Reflectance Recovery %	Cycles to Failure
5	82	78	94.26	770
6	82	77	94.25	865

	PACKAGE STABILITY 2 Weeks @ 125°F			
	Skinning	Phase Separation	Settling	Ease of Remix
5	None	Trace	None	Excellent
6	None	Trace	None	Excellent

EXAMPLE 5

Tests were performed as follows:

1. Viscosity: With a Stormer Viscometer according to ASTM D562-81.

2. Acidity: pH was determined using a Beckman model H-2, using Federal Test Method Number 141, Method 5111.

3. Grind: Determined using Hegman grind gauge according to ASTM D1210-79.

4. Gloss and Sheen: Determined using Byk Multi-angle reflectometer, according to ASTM D523-80.

5. Scrub resistance: Determined with a Gardner scrub maching according to ASTM D2486-79.

6. Contrast Ratio: Determined according to Federal Test Method Standard Number 141, Method 4122.1 and ASTM D2805-80.

7. Flow, Leveling and Sag Resistance: Determined according to ASTM D2801-69. The relative flow and leveling is reported on a

scale of 1 to 10 with 10 representing excellent and 0 representing poor flow.

8. Stain Removal: Determined by a modified version of ASTM D2198-84 in which films are applied to a Lenata card drawn down with a Bird-type applicator, 8-mil wet and dried at least ten days. The ease of removal of each stain using 20 hand washing cycles with a cheesecloth pad wet with Ivory soap or Fantastick household cleaner is recorded on a 1-5 scale as follows: 5 = 100% removal; 4 = 75% removal, 3 = 50% removal; 2 = 25% removal and 1 = 0% removal.

9. Water Spotting: Determined by a modified version of ASTM D2571 with flims applied with a drawn-down bar, 4-mil wet and dried at least seven days. Then a draw of water is put on the film and allowed to stand for 30 minutes before being blotted dry. The film is examined for softening and again after 24 hours drying for extent of recovery.

10. Blocking: Determined according to a modified version of ASTM D2793-69. Films are applied to Lenata form 7B using a draw-down bar to give a 4-mil wet film and dried at least ten days. One inch strips are placed face-to-face under a weight providing one pound per square inch pressure in an oven set at 120°F for one hour. The assembly is removed, cooled and pulled apart noting any transfer of paint from one surface to the other.

11. Low Temperature Coalescence Test: A three mil wet film of the test paint is cast on a sealed Lenata Form 7B chart, using paint which has been pre-conditioned at 50-55°F. The films are allowed to dry in a cold tomb or chamber maintained at 45-5°F overnight with free passange of air. A film (3-mil wet) of an alkyd based semi-gloss paint is then drawn down across the paint film in a way that some area of the semi-gloss is also covering the bare chart. After 48 hours drying at ambient laboratory conditions, 60° gloss readings are made of the semi-gloss over both the test paint area and the bare chart area. The ratio of these two readings (gloss over test paint/gloss over bare chart) is calculated. Ratios around 1.00 indicate good low temperature

coalescence of the test paint.

Three paint formulations containing texanol (Coalescent 3) and isodecyl benzoate (Coalescent 1) were prepared. The first paind formulation was made by blending the following components into a slurry:

Ingredients	Pounds
Propylene glycol	70.0
Tamol SG-1	12.0
Nopco NDW	2.0
Water	45.0
Super Ad-it	1.0
Tri-Pure R-900	210.0
ASP-170	45.0

Texanol and isodecyl benzoate were mixed into separate aliquots of this formulation on a a high speed mill for seven minutes. Then the slurry was let down into the following mixture to prepare the test paint formulations.

	4% Coalescent		8% Coalescent		12% Coalescent	
	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate
Isodecyl Benzoate	9.2	0	18.3	0	27.7	0
Texanol	0	9.2	0	18.3	0	27.7
Water	25.0	25.0	25.0	25.0	25.0	25.0
Rhoplex AC-490	497.2	497.2	497.2	497.2	497.2	497.2
Nopco NDW	1.0	1.0	1.0	1.0	1.0	1.0
Ammonia (28%)	1.8	1.8	1.8	1.8	1.8	1.8
Acrysol RM-5]	30.0	30.0	30.0	30.0	30.0	30.0
Water]Premix	21.0	21.0	21.0	21.0	21.0	21.0
Ammonia (28%)]	1.0	1.0	1.0	1.0	1.0	1.0
Water]	21.0	21.0	21.0	21.0	21.0	21.0
Water	40.2	40.2	30.5	30.5	20.6	20.6

PVC = 25.5%
Volume solids = 31.95%

Paint	Coalescent & Level	Stomer Viscosity (K.U.'s)	pH	Hegman Grind	Weight per Gallon	Reflectance	Contrast Ratio
1	1 - 4%	94	8.5	7.5	10.27	90.5	0.983
2	1 - 8%	101	8.5	7.5	10.27	90.5	0.989
3	1 - 12%	99	8.5	7.5	10.29	92.0	0.978
4	3 - 4%	90	8.5	7.5	10.27	90.5	0.983

Paint	Coalescent & Level	Stomer Viscosity (K.U.'s)	pH	Hegman Grind	Weight per Gallon	Reflectance	Contrast Ratio
5	3 - 8%	96	8.5	7.5	10.28	91.0	0.989
6	3 - 12%	97	8.5	7.5	10.26	91.0	0.989
7	none	89	8.3	7.5	10.25	91.0	0.988

Paint	Coalescent & Level	P/T	Scrub Cycles	Water Spotting	60° Gloss (Hours) 24	48	85° Sheen (Hours) 24	48	Blocking
1	1 - 4%	5	387	OK	45	41	82	83	Passed
2	1 - 8%	5	419	OK	43	35	83	81	Passed
3	1 - 12%	5	483	OK	53	48	87	86	5% Trans.
4	3 - 4%	5	268	OK	43	39	83	80	Passed
5	3 - 8%	5	384	OK	53	50	85	85	Passed
6	3 - 12%	5	407	OK	31	29	80	78	Passed
7	none	5	318	OK	56	55	87	87	Passed

Paint	Coalescent & Level	Low Temperature Coalescence Test	Color Accept.	— Stain Removal — Pencil P	I	Crayon P	I	Lipstick P	I	Ballpoint P	I
1	1 - 4%	1.07	Equal	4	5	5	3	5	5	4	4
2	1 - 8%	1.19	Darker	5	5	4	5	5	5	4	4
3	1 - 12%	1.09	Darker	5	5	5	5	5	5	3	3
4	3 - 4%	*	Lighter	5	5	4	5	5	5	4	5
5	3 - 8%	1.04	Lighter	5	4	4	4	5	5	4	4
6	3 - 12%	1.02	Lighter	4	4	4	4	5	5	3	3
7	none	1.08	Std.	5	5	5	4	5	5	2	2

*sample inadvertently omitted from test.

The second paint formulation was made by blending the following components into a slurry:

Ingredients	Pounds
Natrosol 250MBR	5.0
Ethylene glycol	33.4
Water	200.0
Tamol 850	8.0
Super Ad-it	6.0
Nopco NDW	2.0
Ti-Pure R-902	225.0
Al-Sil-Ate NC	2.0

Texanol and isodecyl benzoate were mixed into separate aliquots of this formulation on a high speed mill for seven minutes. Then the slurry was let down into the following mixture to prepare the test paint formulations:

	3% Coalescent		6% Coalescent		9% Coalescent	
	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate
Isodecyl Benzoate	7.2	0	14.0	0	21.6	0
Texanol	0	7.2	0	14.0	0	21.6

	3% Coalescent		6% Coalescent		9% Coalescent	
	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate
Rhoplex AC-64	396.5	396.5	396.5	396.5	396.5	396.5
Nopco NDW	1.0	1.0	1.0	1.0	1.0	1.0
Water	83.7	83.7	81.4	81.4	84.9	84.9
2.5% Natrosol 250HBR	85.6	85.6	80.7	80.7	69.2	69.2

PVC = 20.2%
Volume Solids = 26.2%

Paint	Coalescent & Level	Stomer Viscosity (K.U.'s)	pH	Hegman Grind	Weight per Gallon	Reflectance	Contrast Ratio
1	1 - 3%	84	8.6	6.5	10.44	90.0	0.983
2	1 - 6%	85	8.7	6.5	10.54	89.5	0.978
3	1 - 9%	86	8.3	6.5	10.55	89.0	0.978
4	3 - 3%	90	8.8	6.5	10.53	90.0	0.978
5	3 - 6%	82	8.9	6.5	10.53	90.5	0.983
6	3 - 9%	89	7.4	6.5	10.53	90.0	0.978
7	none	85	8.8	6.5	10.62	90.0	0.983

Paint	Coalescent & Level	F/T	Scrub Cycles	Water Spotting	60° Gloss (Hours) 24	48	85° Sheen (Hours) 24	48	Blocking
1	1 - 3%	5	266	Softens	11	10	48	46	Passed
2	1 - 6%	5	296	Dulls	13	11	50	45	Passed
3	1 - 9%	5	166	Dulls	21	18	68	61	Passed
4	3 - 3%	5	248	Halo	10	9	43	42	Passed
5	3 - 6%	5	292	Dulls	12	10	39	36	Passed
6	3 - 9%	5	352	Dulls	36	32	80	76	Passed
7	none	5	170	Dulls	10	8	52	50	Passed

Paint	Coalescent & Level	Low Temperature Coalescence Test	Color Accept.	— Stain Removal — Pencil P	Pencil I	Crayon P	Crayon I	Lipstick P	Lipstick I	Ballpoint P	Ballpoint I
1	1 - 3%	0.98	Darker	4	4	5	5	5	5	3	3
2	1 - 6%	0.98	Darker	4	4	5	5	5	5	3	3
3	1 - 9%	0.98	Darker	4	4	5	5	5	5	3	3
4	3 - 3%	0.97	Darker	5	4	5	5	5	5	3	2
5	3 - 6%	1.05	Darker	4	4	5	5	5	5	3	3
6	3 - 9%	1.03	Darker	4	4	5	4	5	5	2	3
7	none	1.02	Std.	4	4	5	5	5	5	3	3

The third paint formulation was made by blending the following components into a slurry:

Ingredients	Pounds
Methyl Carbitol	45.0
Tamol QR 1124	3.0
Triton CF-10	1.8
Foamaster AP	1.5
Ti-Pure R-900	196.0

Texanol and isodecyl benzoate were mixed into separate aliquots of this formulation on a high speed mill for seven minutes. Then the slurry was let down into the following mixture to prepare the test paint formulations:

	10% Coalescent		15% Coalescent		20% Coalescent	
	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate	Texanol	Isodecyl Benzoate
Isodecyl Benzoate	23.1	0	34.6	0	46.2	0
Texanol	0	23.1	0	34.6	0	46.2
Rhoplex HG74A	543.5	543.5	543.5	543.5	543.5	543.5
Foamaster AP	0.5	0.5	0.5	0.5	0.5	0.5
Dowicil 75] Premix	1.6	1.6	1.6	1.6	1.6	1.6
Water]	6.4	6.4	6.4	6.4	6.4	6.4
Water]	15.0	15.0	15.0	15.0	15.0	15.0
Acrysol RM-5]	35.0	35.0	35.0	35.0	35.0	35.0
]Premix						
Water]	15.0	15.0	15.0	15.0	15.0	15.0
Ammonia (28%)]	1.8	1.8	1.8	1.8	1.8	1.8
Water	107.9	107.9	87.4	87.4	75.1	75.1

PVC = 17.2%
Volume Solids = 32.7%

Paint	Coalescent & Level	Stomer Viscosity (K.U.'s)	pH	Hegman Grind	Weight per Gallon	Reflectance	Contrast Ratio
1	1 - 10%	87	8.8	7.0	10.11	89.5	0.983
2	1 - 15%	94	8.9	7.0	10.01	90.5	0.978
3	1 - 20%	103	8.9	7.0	10.03	90.0	0.983
4	3 - 10%	88	8.8	7.0	10.08	89.5	0.978
5	3 - 15%	96	8.8	7.0	10.05	90.0	0.983
6	3 - 20%	103	8.8	7.0	10.02	90.5	0.978
7	none	80	8.8	7.0	10.14	89.5	0.983

Paint	Coalescent & Level	F/T	Scrub Cycles	Water Spotting	60° Gloss (Hours) 24	48	85° Sheen (Hours) 24	48	Blocking
1	1 - 10%	5	106	OK	76	73	92	88	Passed
2	1 - 15%	2	132	OK	80	76	93	91	Passed
3	1 - 20%	0	176	OK	73	80	93	91	Passed
4	3 - 10%	2	282	OK	76	76	92	92	Passed
5	3 - 15%	2	208	OK	77	77	94	92	Passed
6	3 - 20%	0	250	OK	73	76	92	90	Passed
7	none	5	160	OK	72	74	91	90	Passed

Paint	Coalescent & Level	Low Temperature Coalescence Test	Color Accept.	— Stain Removal — Pencil F	I	Crayon F	I	Lipstick F	I	Ballpoint F	I
1	1 - 10%	0.83	Lighter	5	5	5	5	5	5	5	5
2	1 - 15%	0.90	Lighter	4	4	5	5	5	5	5	5
3	1 - 20%	0.82	Lighter	5	5	5	5	5	5	5	5
4	3 - 10%	0.77	Equal	5	4	5	5	5	5	5	5
5	3 - 15%	0.73	Darker	4	4	5	5	5	5	5	5
6	3 - 20%	0.69	Darker	4	4	5	5	5	5	5	5
7	none	0.55	Std.	5	5	5	5	5	5	5	5

EXAMPLE 6

Tests were performed as follows:

1) Compare 2 paints made exactly alike but using isodecyl benzoate and N-Butyl benzoate at an 8% level by weight based on the emulsion solids. Different tests were performed to compare various properties.

2) Formulation: V-4 (pigment slurry)

	LBS.	GALS.
Water	278.97	33.49
Natrosol MBR	5.5	0.51
AMP-95	1.0	0.13
KTPP	1.5	0.08
Ethylene glycol	13.9	1.49
Nopcosperse 44	5.1	0.50
Igepal Co430	1.5	0.18
Igepal Co630	3.3	0.38
Foamaster SA-1	2.0	0.28
RR551 W.D. Lecithin	2.2	0.25
Tipure R-931	155.0	5.12
Zeolex 80	25.0	1.43
Calite 281	46.5	2.42
Vicron 25-11	75.0	3.32
Apex 400	150.0	6.91
Satintone W	50.0	2.28

THINDOWN

V-4A = Isodecyl benzoate

	LBS.	GALS.
Formaster SA-1	1.6	0.23
Isodecyl Benzoate (Velate 262)	7.86	0.99
Wallpol 40-136	178.7	19.75
2 1/2 % Natrosol 250 MBR solution	180.0	21.42
	1184.7	101.16

V-4B = N-Butyl Benzoate

	LBS.	GALS.
Foamaster SA-1	1.6	0.23
N-Butyl Benzoate	7.86	0.94
Wallpol 40-136	178.7	19.75
2 1/2% Natrosol 250 MBR Solution	180.0	21.42
	1184.63	101.11

3) The following charts will indicate test results:

TEST	V-4A	V-4B
Viscosity	104 ku	104 ku
Wt/gallon	11.58	11.68
Hegman Fineness	3 1/2	3 1/2
P.H.	8.5	8.3
Reflectance (003)	.900	.900
C/R (00.5)	.972	.972
C/R (003)	.983	.983
60° gloss	2.8%	2.8%
85° gloss	0.8%	2.8%
Freeze thaw	Passes 4 cycles	Fails 1st cycle
Scrubbibility	52 cycles	73 cycles
Stain resistance	42.7% Ref. retent.	41.3% ref. ret
Yellowing index	.0297	.0671
Odor	Mild and inoccuos	Extremely* pungent and sweet
Cold touch-up	Poor/fair	Fair/good
Cold application		
Room touch-up	Poor/fair	Good
Cold application	74.7% retantion	69.7% retantion
Enamel hold out	10 mil-none	10 mil-none
Mudcracking	20 mil-slight to moderate	20 mil-slight to moderate
	30 mil-severe	30 mil-severe
Coalescance	Air dry ref.-635	Air dry ref.635
	38° ref.655=	38°F ref..650=
	96.95 ret.	97.69% ret.

TEST	V-4A	V-4B
Oven Stability		
P.H.	7.7	7.7
Vis	102 Ku	102 ku
Blocking resistance	No transfer	No transfer
Water resistance	Softens	Softens
	Recovery-full	Recovery-full
	24 hours	24 hours
Color acceptance	Yellow oxide	Yellow oxide
Universal colors	Low shear	Low shear
	Reference-755	Ref. 755
	Yellow oxide	Yellow oxide
	High shear	High shear
	Ref. 755	Ref. 755
	(no change)	(no change)
	Pthalo	Pthalo Green
	Low shear	Low shear
	Reflectance .635	Ref. 640
	Pthalo green	Pthalo green
	High shear	High shear
	Reflectance 640	Reflectance 645
	(0.99%)(color loss)	(0.99%)(color loss)

*odor is commercially unacceptable.

4) Typically, a coalescent retention and hardness development test is used to screen potentially suitable coalescing agents. An example of such a test involved adding 15% of both isodecyl benzoate and N-butyl benzoate to Rohm & Haas HG-74A acrylic emulsion. The addition was on the basis of emulsion solids.

a) Isodecyl benzoate

Film non-homogeneous; completely wrinkled.

b) N-butyl benzoate - film completely homogeneous excellent smoothness and clarity.

Based on this screen test one of ordinary skill in the art would probably dismiss isodecyl benzoate as a potentially suitable coalescing agent.

5) Typically, a minimum film forming temperature test is used to screen potentially suitable coalescing agents. An example of such a test determined minimum film forming temperatures for the N-butyl and isodecyl benzoate in the following latex emulsions:

TYPE	LEVEL	LATEX	MFT
N-butyl benzoate	8% on solids	40-136	Less than 0°C
Isodecyl benzoate	8% on solids	40-136	Less than 0°C
N-butyl benzoate	8% on solids	Flexbond 325	Less than 0°C
Isodecyl benzoate	8% on solids	Flexbond 325	4°C

This test run was according to ASTM-D-02354-06.

Based on this screen test, one of ordinary skill in the art would probably dismiss isodecyl benzoate as a suitable coalescing agent.

6) Test Methods

A) Viscosity - Stormer viscometer according to ASTM-D-562-81.

B) P.H. - Fisher accument model 620.

C) Grind - Hegman Guage, ASTM 1210-79.

D) Gloss -

Sheen - Byk multiangle glossmeter ASTM D523-80.

E) Reflectance and Contrast Ratio - ASTM 2805-80.

F) Scrub Resistance - Gardner Scrub machine ASTM-2486-79.

G) Freeze Thaw - ASTM D-2243-82.

H) Wt/gallon - ASTM D-1475-60.

I) Stain Resistance - A 7 mil wet film is applied to a leneta scrub chart (P-121-10N) and dried for 7 days at ambient temperature. A reflectance is then taken and a 3 mil wet film of Leneta ST-1 pigmented staining medium is applied over the area from which the reflectance was taken.

Panel is then put in 120°F oven for 24 hours. Panel is then removed from oven and excess stain is blotted off. Panel is washed using appropriate sponge in Gardner Scrub apparatus with IOcc of "Fantastik" commercial cleanser. Twenty-five cycles are run and panel is removed and rinsed in water to remove any excess stain. Panel is allowed to air dry and a reflectance is run over area which

divided into the reflectance after washing has occurred and percent reflectance retention is obtained.

J) Yellowing Index - Method 6131 of federal test method STD 141.

K) Odor - The interior of a one gallon paint can is coated liberally and immediately sealed for 72 hours. Container is then opened and severity of odor is determined.

L) Touch-Ups

1) Cold temperature applied - cold temperature touch-up

An upson board panel, paint to be tested and roller cover are put into refrigerator at 38°F and conditioned for 24 hours. One coat is rolled on and allowed to dry in refrigerator for 24 hours. The above process is then repeated for 2nd coat and dried for another 24 hours. A good quality one inch brush is put into refrigerator with paint sample that was used to roll out panels. After 24 hours the panel is touched up and left in refrigerator for another 24 hours. After this period panel is removed and panel is rated visually.

2) Cold temperature applied - room temperature touch-up

An upson board panel, paint to be tested and roller cover are put into refrigerator at 38°F and conditioned for 24 hours. One coat is rolled on and allowed to dry in the refrigerator for another 24 hours. Panels are then removed from refrigerator and allowed 4 hours to come to ambient room temperature (72° to 75°F). Panels are then touched up with the test paint that was applied by roller but which was kept at ambient room

roller but which was kept at ambient room temperature. After 24 hours dry panel is rated visually.

M) Enamel Holdout - A 4 mil wet film is cast on a Leneta form 7B chart and dried 48 hours. A 3 mil wet alkyd semi-gloss is drawn down perpendicular to the test paint and dried 3 days. Enamel holdout is determined by the ratio of the gloss of the alkyd over the test paint divided by the gloss of the alkyd over the chart only.

N) Mudcracking - A 10, 20 and 30 mil wet film is cast onto a Leneta form WK sealed chart and allowed to dry for 24 hours. Mudcracking is rated visually as to degree of severity.

O) Coalescence - Colorant 888-5511D Pthalo green universal colorant manufactured by Nuodex Inc. is added to a 1/2 pint sample of test paint in the amount of 3 grams. Sample is then put on Red Devil paint shaker for 5 minutes. Tinted sample is then drawn down with .003 bird applicator on Leneta form WK chart and dried for 24 hours at which time a reflectance reading is taken.

The remainaing paint is then put into refrigerator with a form WK Leneta chart and the .003 bird applicator and allowed to condition for 24 hours at $38^{\circ}F$.

After this period, paint, chart, and applicator are removed and a drawdown is quickly made and panel is immediately put back into refrigerator and allowed to dry for 24 hours. Panel is then removed and allowed 4 hours to come to ambient room temperature. Reflectance is then taken.

The cold temperature reflectance is then divided into the ambient temperature reflectance and a percentage is established. The higher percentage

indicates the best coalescense.

P) Oven Stability - A full 1/2 pint sample of each test paint is put into a 120° oven for 30 days. Samples are then removed and allowed to cool to ambient temperature for 24 hours. Viscosity and P.H. are then checked and compared against the initial readings.

Q) Blocking Resistance - According to a modified version of ASTM D-2793-69 films are applied to a Leneta chart form 7B at a 4 mil wet film and dried for 10 days. One inch strips of the coated panel are placed face to face under a weight providing one pound per square inch pressure and put into a 120°F oven for one hour. The assembly is then removed, cooled and pulled apart, noting the transfer of paint from one surface to the other, if this occurs.

R) Water Resistance - According to a modified version of ASTM D-2571, film is appalied onto a clear glass panel with a 4 mil wet drawdown bar and dried at ambient temperature for 7 days. A drop of deionized water is put on the film, covered with a watch glass and allowed to stand for 30 minutes before being blotted dry. The film is then examined for softening, and again after 24 hours drying for extent of recovery.

S) Color acceptance - For this test two Universal colorants are checked separately. They are Nuodex 888-1810FC yellow oxide and 888-5511D Pthalo green. Three grams of each colorant is added to separate 1/2 pint cans and filled with test paint. Cans are then put on Red Devil shaker for 5 minutes. Each color is then applied to a Leneta form WK chart using a good quality 2 inch nylon brush. Not more than 10 strokes of the brush will be used on these

panels which will be identified as low sheer panels.

The same paints will be applied to separate form WK charts using 50 brush strokes for each panel. These panels will be identified as high sheer panels.

All panels will be dried for 24 hours and a reflectance reading will then be taken on each panel.

If the reflectance on the high sheer panel is higher than the low shear panel, it is indicative of color loss. A percentage will be obtained by dividing the higher reflectance reading into the lower reading.

If the reflectance on the high shear panel is lower than the low sheer panel it is indicative of color development.

A percentage will be obtained by dividing the higher reading into the lower reading.

Another use of the present compound is as plastisols. In essence, a plastisol is a dispersion of a synthetic elastomer in a plasticizor together optinally with fillers, pigment and stabilizers. The plasticizer compounds enable the elastomer being plasticized to be sufficiently flexible to be formed into articles. In the absence of the plasticizer, the elastomers are too rigid to be useful. A typical formula would be as follows:

Polyvinyl chloride	100 parts
Compound of Present Invention	50 parts
Stabilizer	3 parts

In preparing these plastisols, normally the polymer will constitute from about 60 to about 75 percent by weight, the present compound about 30 to about 40 percent by weight and the stabilizer about one to about five weight percent.

Of particular use with plastisols are polyvinyl chloride, polyvinyl acetate and polyacrylates. Other polymers can also be used.

The choice of the stabilizers is dependent on the polymer, as stabilizers known as useful with the specific polymers can also be used in this application. Typical of these materials are barium and cadmium phenalate.

In order to demonstrate the usefulness of the present compounds as plastisols, thermogravimetric analyses, gel point, viscosity and film volatility are performed. The present compounds are able to meet the requirement of all of the listed tests so as to function as plastisols.

Another important utility of the present compounds is in the preparation of caulks. A caulk must be able to stay in place once it is applied to fill a space, normally a crack. Caulks are water based systems.

The major component of a caulk is the polymer emulsion. This component will generally constitute a minimum of 90 percent by weight of the caulk. A highly desirable emulsion for use in the caulk is an acrylic emulsion. Other significant components are the plasticizer and the thickener. These components can constitute up to three weight percent of the caulk composition.

In a typical caulk composition, the present compound would be premixed with the lesser components, i.e., defoamers, ethylene gylcol, sodium lauryl sulfate, etc. and then with a portion of the acrylic emulsion for a few minutes. Then this mixture would be mixed with the remainder of the acrylic emulsion, the defoamer and ammonium hydroxide for a few additional minutes. A typical formula is:

Premix

Solid sodium lauryl sulfate	1.2 pounds
Ethylene glycol	2.6
Compound of present invention	13.0
Defoamer	1.6

This premix is then mixed for five minutes with:

Acrylic emulsion	338.4 pounds
Thickener	15

This mixture is then mixed for an additional five minutes with:

Acrylic emulsion	507.5 pounds
Ammonium hydroxide	3.2
Defoamer	1.6

This product is an excellent caulk. As can be seen from this formulation, the presence of the components other than the present compounds does not vary from the preparation of known caulk formulations and, thus, is within the skill of the art. The important fact is that the new compounds of this invention can be used in the preparation of caulks.

In addition to foregoing uses of the present compounds as coalescing agents, plastisols and in the preparation of caulks, these compounds have several other utilities:

1. a purge for polyurethane equipment;
2. a plasticizer for polyurethane;
3. a solvent for alkyls in the preparation of coatings; and
4. a plasticizer for polyvinyl acetate copolymer adhesives.

CLAIMS:

1. In the method of the preparation of paint compositions by the mixing of latex, pigment and adjuvents thereof, the improvement which comprises incorporating into the paint composition a coalescing amount of an ester of benzoic acid having from about 10 to about 12 carbon atoms in its ester moiety.

2. The method of Claim 1 wherein the coalescing amount of the ester is present in an amount of from about 4 to about 12 precent by weight of the paint composition.

3. The method of Claim 1 wherein the ester of benzoic acid is an aliphatic hydrocarbon.

4. The method of Claim 1 wherein the ester of benzoic acid is isodecylbenzoate.

5. The method of Claim 1 wherein the ester of benzoic acid is decylbenzoate.

6. The method of Claim 1 wherein the ester of benzoic acid is isoundecyl benzoate.

7. The method of Claim 1 wherein the ester of benzoic acid is undecyl benzoate.

8. The method of Claim 1 wherein the ester of benzoic acid is isododecyl benzoate.

9. The method of Claim 1 wherein the ester of benzoic acid is dodecyl benzoate.

10. A paint composition having a mixture of latex, pigment and adjuvents thereof, the improvement which comprises incorporating into the paint composition a coalescing amount of an ester of benzoic acid having from about 10 to about 12 carbon atoms in its ester moiety.

11. The paint composition of Claim 10 wherein the coalescing amoaunt of the ester is present in an amount of from about 4 to about 12 percent by weight of the paint composition.

12. The paint composition of Claim 10 wherein the coalescing amount of the ester of benzoic acid is an aliphatic hydrocarbon.

13. The paint composition of Claim 10 wherein the ester of benzoic acid is isodecyl benzoate.

14. The paint composition of Claim 10 wherein the ester of benzoic acid is decyl benzoate.

15. The paint composition of Claim 10 wherein the ester of benzoic acid is isoundecyl benzoate.

16. The paint composition of Claim 10 wherein the ester of benzoic acid is undecyl benzoate.

17. The paint composition of Claim 10 wherein the ester of benzoic acid is isododecyl benzoate.

18. The paint composition of Claim 10 wherein the ester of benzoic acid is dodecyl benzoate.

19. A plastisol composition comprising an elastomer and a plasticizing amount of an ester of benzoic acid having from about 10 to about 12 carbon atoms in its ester moiety.

20. The plastisol composition of Claim 19 wherein the ester of benzoic acid is present in an amount of from about 4 to about 12 percent by weight of the plastisol composition.

21. The plastisol composition of Claim 19 wherein the ester of benzoic acid is an aliphatic hydrocarbon.

22. The plastisol composition of Claim 19 wherein the ester of benzoic acid is isodecylbenzoate.

23. The plastisol composition of Claim 19 wherein the ester of benzoic acid is decylbenzoate.

24. The plastisol composition of Claim 19 wherein the ester of benzoic acid is undecyl benzoate.

25. The plastisol composition of Claim 19 wherein the ester of benzoic acid is isoundecyl benzoate.

26. The plastisol composition of Claim 19 wherein the ester of benzoic acid is dodecyl benzoate.

27. The plastisol composition of Claim 19 wherein the ester of benzoic acid is isododecyl benzoate.

28. In the method of the preparation of plastisol compositions by the mixing of an elastomer and a plasticizing amount of an ester of benzoic acid having from about 10 to 12 carbon atoms in its ester moiety.

29. The method of Claim 28 wherein the ester of benzoic acid is isodecyl benzoate.

30. The method of Claim 28 wherein the ester of benzoic acid is decyl benzoate.

31. The method of Claim 28 wherein the ester of benzoic acid is undecyl benzoate.

32. The method of Claim 28 wherein the ester of benzoic acid is isoundecyl benzoate.

33. The method of Claim 28 wherein the ester of benzoic acid is dodecyl benzoate.

34. The method of Claim 28 wherein the ester of benzoic acid is isododecyl benzoate.

35. A caulk composition having a mixture of polymer emulsion and adjuvents thereof, the improvement which comprises incorporating into the caulk composition an ester of benzoic acid having from about 10 to about 12 carbon atoms in its ester moiety.

36. The caulk composition of Claim 35 wherein the ester of benzoic acid is isodecyl benzoate.

37. The caulk composition of Claim 35 wherein the ester of benzoic acid is decyl benzoate.

38. The caulk composition of Claim 35 wherein the ester of benzoic acid is undecyl benzoate.

39. The caulk composition of Claim 35 wherein the ester of benzoic acid is isoundecyl benzoate.

40. The caulk composition of Claim 35 wherein the ester of benzoic acid is dodecyl benzoate.

41. The caulk composition of Claim 35 wherein the ester of benzoic acid is isododecyl benzoate.

42. In the method of the preparation of a caulk composition by the mixing of a polymer emulsion and an amoaunt of an ester of benzoic acid having from about 10 to 12 carbon atoms in its ester moiety.

43. The method of Claim 42 wherein the ester of benzoic acid is isodecyl benzoate.

44. The method of Claim 42 wherein the ester of benzoic acid is decyl benzoate.

45. The method of Claim 42 wherein the ester of benzoic acid is undecyl benzoate.

46. The method of Claim 42 wherein the ester of benzoic acid is isoundecyl benzoate.

47. The method of Claim 42 wherein the ester of benzoic acid is dodecyl benzoate.

48. The method of Claim 42 wherein the ester of benzoic acid is isododecyl benzoate.

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(57) Abstract

This application discloses the use of esters of benzoic acid having from about 10 to about 12 carbon atoms in the ester moiety as coalescent agents for paint compositions and for use in the preparation of plastisols and caulks.

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INTERNATIONAL SEARCH REPORT

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I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

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II. FIELDS SEARCHED

Minimum Documentation Searched [7]

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IPC[4]	C 08 K; C 08 L; C 09 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	FR, A, 2026170 (J.R. GEIGY S.A.) 11 September 1970 see claims; page 4, lines 33-39; examples 4-6,8,13,14 --	19,28,35, 42
A	GB, A, 1317689 (UTVECKLINGS AB TENET) 23 May 1973 --------	

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IV. CERTIFICATION

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6th December 1988	28. 12. 88
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/12/88
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